# Heating Simulation of Multilayer Preforms

**PH. LEBAUDY, J. GRENET**

L.E.C.A.P., Faculté des sciences de Rouen, BP 118, 76134 Mont-Saint-Aignan Cedex, France

**ABSTRACT:** In the area of beverage packaging, the barrier properties (to gases, water, organic vapors/flavors) are parameters of great importance. For poly(ethylene terephtalate) (PET), largely used in bottling, the improvement of these barrier properties upon biaxial orientation is a direct result of both the level of crystallinity as well as the orientation of the material. However, even with higher crystallinity and orientation for some applications, the PET barrier properties are not adequately efficient and thus multilayer polymer materials must be used to make the bottles. During plastic-forming processes, the semifinished multilayer thermoplastic products (such as a preform) must be heated to a rubberlike state. Experiments on PET reveal that temperatures either below or close to the glass transition ($T_g$) are essential to achieve principally oriented glassy structure and that the crystalline structure could be enhanced as well by thermal or high-drawing treatments. Because of the great differences in the stretching ratio inside the preform and the thermomechanical behavior of the materials, a good stretching process requires that the material have a nonuniform temperature profile. A model is developed to calculate temperature distribution in multilayer preforms. This model is a useful tool for understanding the heating stage of thermoplastic products and is suitable to control and optimize industrial processes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2683–2689, 2001

**Key words:** polymer processing; multilayers; heat transfer; infrared heating

## INTRODUCTION

Knowledge of temperature distributions in a polymeric medium undergoing various heat treatments is of fundamental importance in forming processes. Indeed, when solid and amorphous PET is biaxially oriented, two things take place. First, some of the stretched chains that were initially disoriented arrange into crystalline structure. Both the stretching action and the temperature at which it occurs determine the level of crystallinity. When crystallization occurs only with temperature, the resulting crystalline fraction is characterized by a spherulitic morphology, in which the resulting cooled part would be opaque. Without stretching, of course, the crystallites that are formed become sufficiently large to diffract light. When the crystallinity is formed during the orientation step, however, the part remains transparent because the size of the crystallites that are formed remains smaller than the wavelength of light. Second, the crystallites line up, as it were, in a crisscross fashion (as a result of the force of stretching), which results not only in increased strength for the part but also in better barrier properties.[1] These two phenomena usually take place at the same time and depend on temperature. In biaxial-stretch blow molding of bottles the outer and inner ratios λ differ by

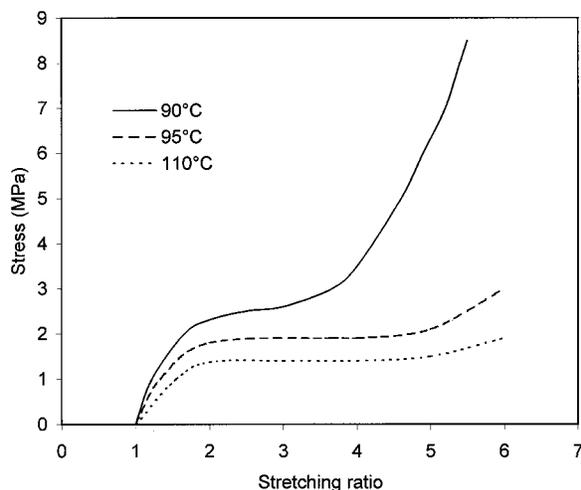**Figure 1** Stress versus stretching ratio for different temperatures.

more than 50% during the stretching ($\lambda_{out}$ = 4 to $\lambda_{in}$ = 5). To ensure good uniformity of the stress distribution in the width of the bottle, it is necessary to deliberately induce a nonuniform profile of temperature throughout the preform before blowing. Indeed, as shown in Figure 1, which represents the thermomechanical behavior of PET,[2] a constant level of stress requires an increase of temperature when the level of strain increases. An example of such a profile limiting the inhomogeneity of stress is shown in Figure 2.[3] These temperature profiles are reached after a 20-s heating time (Fig. 2, curve a) and a 3-s transient time (Fig. 2, curve b).

Today in the area of beverage packaging, the barrier properties (to gases, water, organic vapors/flavors) are crucial parameters: the higher the crystallinity, the better the barrier. For some cases, even with a good optimization of the process, the PET barrier properties are not adequately efficient and, thus, multilayer polymer materials are used (e.g., PET/EVOH/PET or PET/PAmxd6/PET). However, insertion of a middle layer between two layers of PET, for instance, modifies the heating stage of the multilayer preform just before the biaxial orientation, which is a very delicate operation.

The present work presents a numerical model used to determine the temperature distribution in multilayer preform heating by means of infrared radiation. This model takes into account the properties of quartz radiators (distribution of the radiation intensity with wavelength), the optical

characteristics of the materials (PET, EVOH, PA mxd6), and the eventual modifications of the optical properties, which can occur during the thermal process (scattering parameters for semicrystalline polymers).[3]

## EXPERIMENTAL

### Materials and Infrared Interactions

The usual mechanisms of heat transfer by infrared radiation are described in a previous study[3] and are outside the scope of this work. It is sufficient to notice than in plastic processings, quartz radiators are used as infrared radiation sources. These radiators can be used in the large temperature range of 1000 to 2900 K. A change in temperature leads to a change in the distribution of the radiation intensity with wavelength (Fig. 3).

To describe the spectral absorption characteristics of the materials, the Lambert–Bouguer law is used here. For practical considerations, it was found to be advantageous to describe the absorption behavior in terms of penetration depth $E_\lambda$, instead of the absorption coefficient. The spectral radiative flux $\Phi_\lambda(x)$ at point $x$ is given by

$$\Phi_\lambda(x) = I_0\exp(-x/E_\lambda) \tag{1}$$

where $x$ is the thickness from the illuminated outer face of the preform, $I_0$ is the radiation intensity at $x = 0$, and $E_\lambda$ is the material spectral
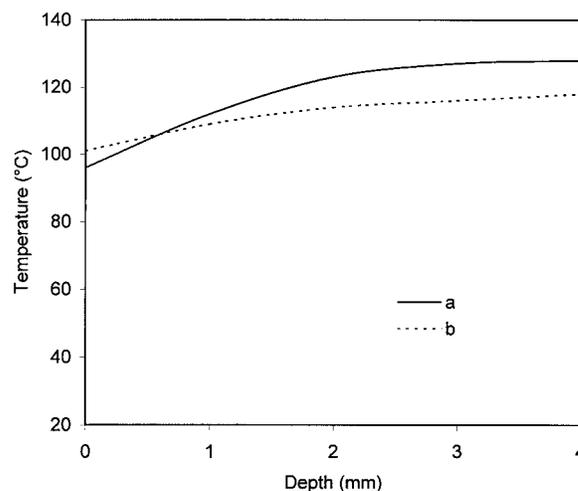


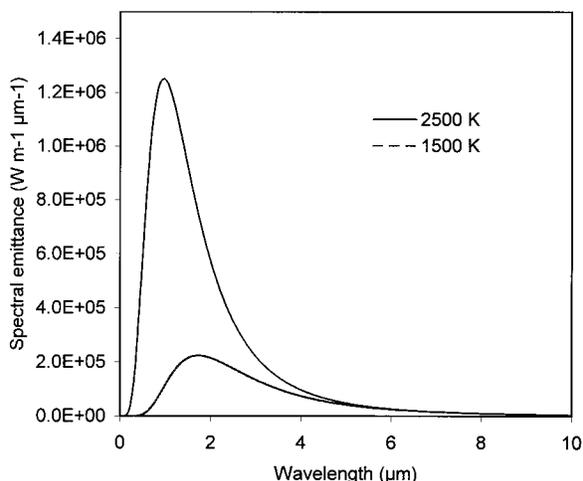**Figure 2** Temperature profile versus depth: (a) end of heating; (b) after a 3-s transient time.

**Figure 3** Spectral emittance of radiation versus wavelength at two temperatures.



**Figure 5** Comparison of diffusion coefficients between amorphous, low-crystallinity, and high-crystallinity plates.

penetration depth. The variations of penetration depth with wavelength for glassy PET, EVOH, and nylon samples are reported in Figure 4. When the material is a semicrystalline polymer, scattering could occur during the heating stage. In this case, the assumption that the path of the radiation beam through the material is rectilinear is no longer justified, and then it is not possible to use the Lambert–Bouguer law to describe the radiative flux behavior. Therefore, to calculate this radiative flux inside the semicrystalline polymer, a four-flux model was used. The spectral coefficients required for this calculation are the absorptivity $A_\lambda$, the reflectance $R_\lambda$, the transmittance $T_\lambda$,
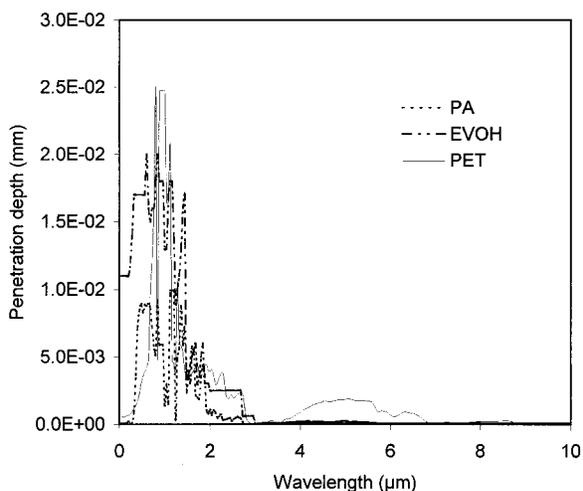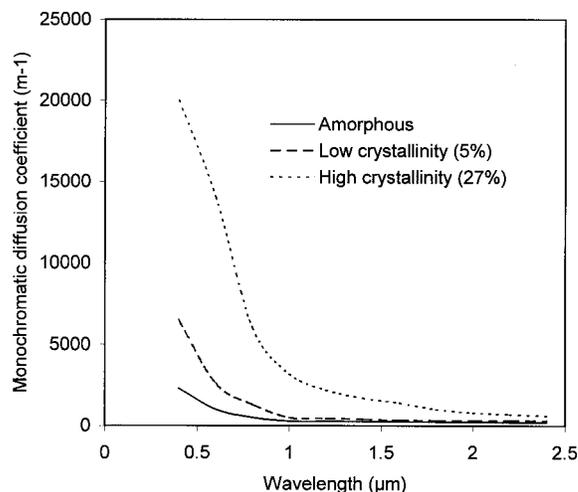
and the scattering coefficient $\sigma_\lambda$. For example, following Denis et al.,[4] in PET the variations of the scattering coefficient $\sigma_\lambda$ with the degree of crystallinity $X_c$ can be expressed by the following behavioral law:

$$\sigma_\lambda(X_c) = \frac{C_1 e^{C_2 \lambda} X_c}{\lambda^4} \qquad (2)$$

where $\lambda$ is the wavelengh and $C_1$ and $C_2$ are two constants. Figure 5 shows a comparison between diffusion coefficients of amorphous, low-crystallinity, and high-crystallinity plates. The crystalline fraction $X_c$ is calculated using Ozawa–Billon's theory,[5–7] which suitably describes the crystallization kinetics of the material when the process proceeds under nonisothermal conditions
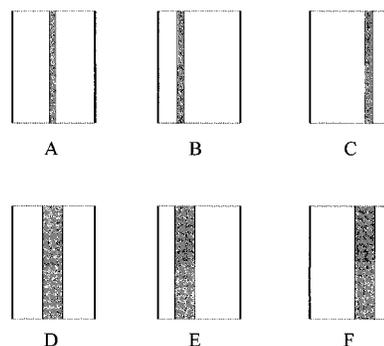


**Figure 4** Penetration depth versus wavelength for PET, EVOH, and PA films.



**Figure 6** Position and thickness of the middle layer.

**Table I   Thermal Parameters of the Oven**

| $T_r$ | Radiator temperature | 1500 and 2500 K |
|---|---|---|
| $R_i$ | Radiator irradiance | 19,000 and 50,000 W m$^{-1}$ |
| $C_0$ | External convective parameter | 70 W m$^{-2}$ K$^{-1}$ |
| $C_i$ | Internal convective parameter | 5 W m$^{-2}$ K$^{-1}$ |
| $T_0$ | External ambient temperature | 30°C |
| $T_i$ | Internal anbient temperature | 50°C |
| $t_t$ | Total simulated time | 20 s |

and when the rate of either cooling or heating changes.

### The Heating Problem

For the sake of simplicity, in this model we consider the equation for unidimensional non-steady-state heat conduction with two location-dependent heat sources[8,9]:

$$\frac{\partial^2 T}{\delta x^2} - \frac{1}{a}\frac{\partial T}{\partial t} + \frac{S(x)}{k} + \frac{\Delta H_c}{aC_p}\frac{\partial \alpha(x)}{\partial t(x)} = 0 \quad (3)$$

where $T$ is the temperature; $t$ is the time; $k$ is the thermal conductivity; $a$ is the thermal diffusivity; $x$ is the depth; $S(x)/k$ is the first location-dependent heat source, which corresponds to the infrared absorption; and

$$\frac{\Delta H_c}{aC_p}\frac{\partial \alpha(x)}{\partial t(x)}$$

is the second location-dependent heat source, induced by the material crystallization enthalpy, where $\Delta H_c$ is the crystallization enthalpy, $C_p$ is the specific heat capacity, and $[\partial \alpha(x)/\partial t(x)]$ is the evolution of the transformed fraction. (This heat source is taken into account only when the material goes through the crystallization temperature range. In this case, the measurement of the evolution of the transformed fraction $[\partial \alpha(x)/\partial t(x)]$ gives the value of the source.)

The first heat-source transfer equation $S(x)$ induced by infrared absorption is highly dependent on the optical properties of the material.[10] For amorphous polymer the spectral heat source $S_\lambda(x)$ is given by the divergence of the spectral radiative flux $\Phi_\lambda(x)$:

$$S_\lambda(x) = -\frac{d\Phi_\lambda(x)}{dx} = -\frac{d[(I_0 \exp(-x/E_\lambda))]}{dx} \quad (4)$$

For semicrystalline polymer the spectral radiative flux is the summation of two collimated
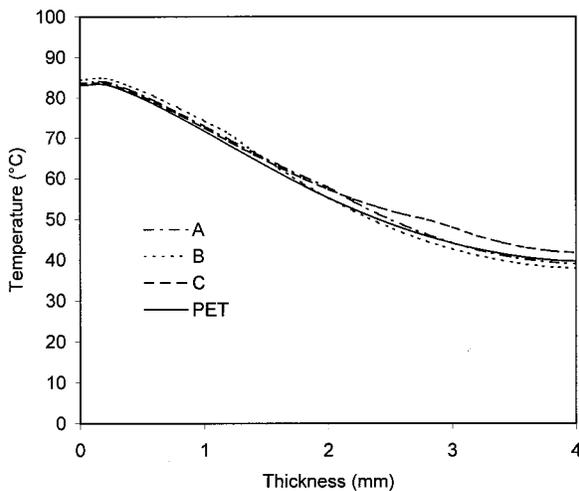


**Figure 7**  Profile temperature on PET/PA/PET preform heated by radiator at $T = 1500$ K (thin layer).
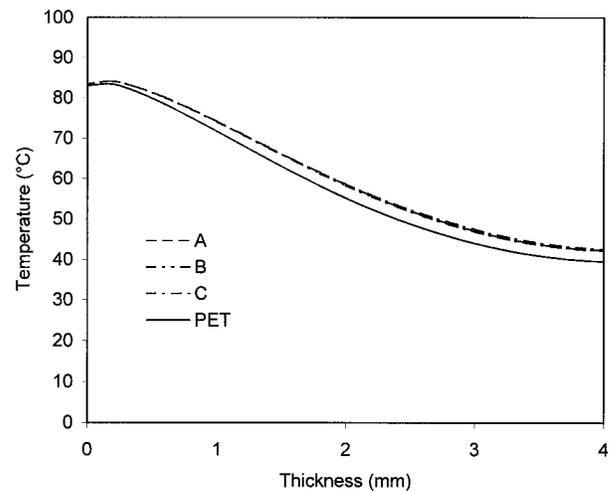


**Figure 8**  Profile temperature on PET/EVOH/PET preform heated by radiator at $T = 1500$ K (thin layer).
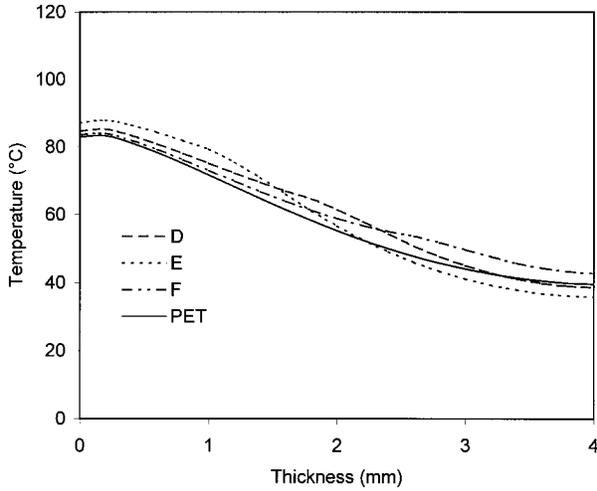
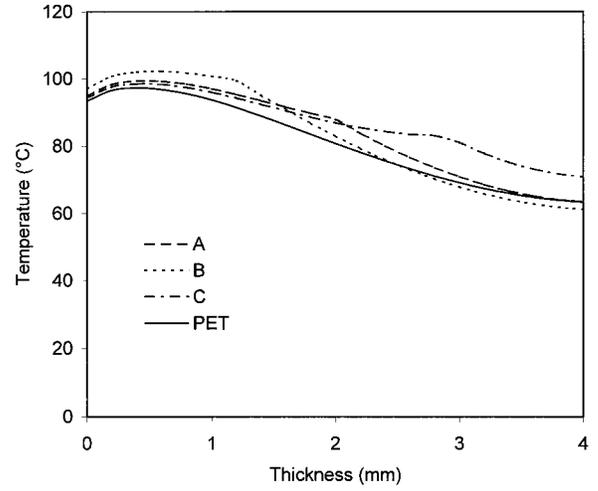**Figure 9** Profile temperature on PET/PA/PET preform heated by radiator at $T = 1500$ K (thick layer).



**Figure 11** Profile temperature on PET/PA/PET preform heated by radiator at $T = 2500$ K (thin layer).

fluxes $I_\lambda^+$ and $I_\lambda^-$ and two isotropic irradiances $L_\lambda^+$ and $L_\lambda^-$, which leads to a four-flux model.[11] The spectral radiative flux is

$$S_\lambda(x) = -\frac{d\Phi_\lambda(x)}{dx} = -\frac{d[(I_\lambda^+ - I_\lambda^-) + \pi(L_\lambda^+ - L_\lambda^-)]}{dx} \tag{5}$$

Because 90% of the total energy given by the radiator is emitted between $\lambda_1 = 0.5\lambda_{max}$ and $\lambda_2 = 5\lambda_{max}$, where $\lambda_{max}$ (the maximum wavelength of the spectral emittance) is given by Wien's law,

the heat source $S(x)$ for all the materials is given by

$$S(x) = \int_{\lambda_1}^{\lambda_2} S_\lambda(x)\, d\lambda \tag{6}$$

Introduced into eq. (3), this expression for $S(x)$ leads to a unidimensional non-steady-state heat-conduction equation that has no analytical solutions. However, the problem was solved by using an explicit numerical method with finite differences. Application of this program is now illus-
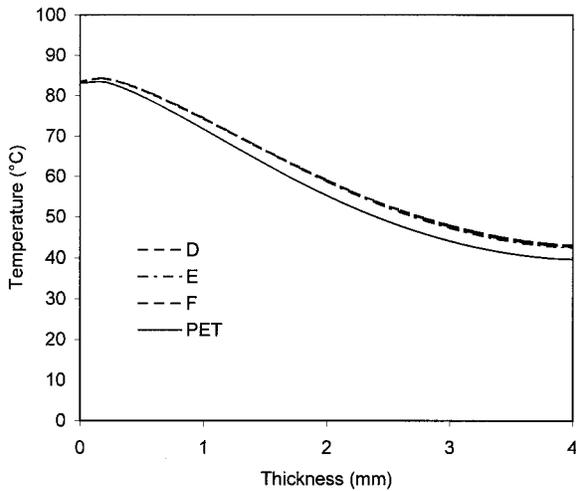


**Figure 10** Profile temperature on PET/EVOH/PET preform heated by radiator at $T = 1500$ K (thick layer).
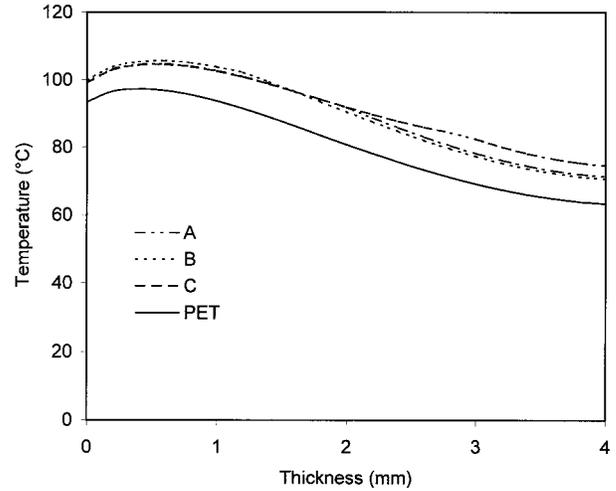


**Figure 12** Profile temperature on PET/EVOH/PET preform heated by radiator at $T = 2500$ K (thin layer).

trated by calculations of the time and space dependence of temperature in multilayer preforms undergoing various heat treatments.

## RESULTS

It is very difficult to manage accurately the thickness and the position of the middle layer during the preform injection. From experimental results on a 4-mm-thick preform we emphasize six significant cases (Fig. 6), three cases with a thin middle layer (0.2 mm), called A, B, C, and three cases with a thick middle layer (0.8 mm), called D, E, and F, respectively. All the temperature profiles of the multilayer preform are compared with the temperature profile of a PET preform. To best understand multilayer influence, the simulations were performed with the same thermal parameters. This set of parameters, as reported in Table I, was chosen to be realistic for an industrial process without any extreme conditions. In Figures 7–10 we report computed temperature profiles of a multilayer preform heated with a radiator temperature of $T = 1500$ K and an irradiance of $R_i = 20,000$ W m$^{-2}$. At this temperature, the radiator emits 75% of its energy between 2 and 10 $\mu$m. These wavelengths are located in the high-absorption region of the three polymers (Fig. 4) and it is presumed that the total energy, except that reflected at the surface, is absorbed at the preform surface. Despite optimal energy efficiency, this heating method leads to high-temperature gradients in the thickness of the pre-
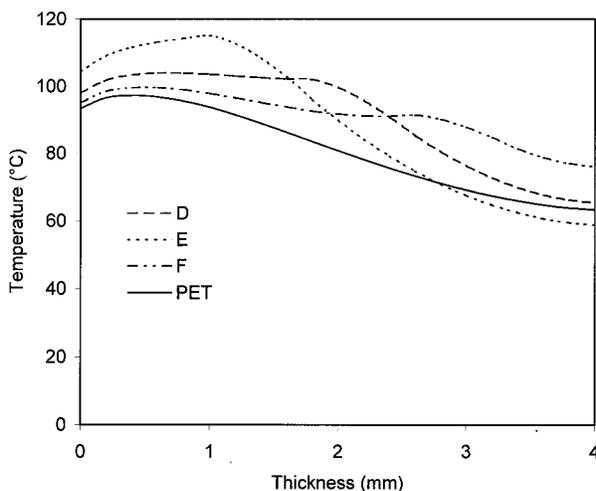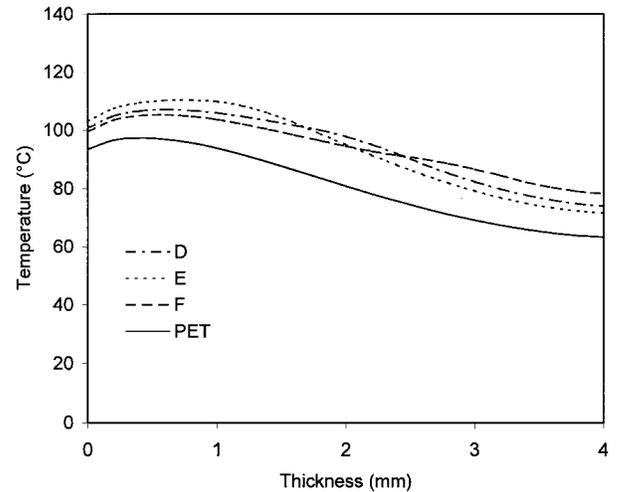


**Figure 14**   Profile temperature on PET/EVOH/PET preform heated by radiator at $T = 2500$ K (thick layer).

form. The middle layer (EVOH or PA) does not drastically modify the temperature profiles.

Figures 11–14 show the temperature profiles for a radiator temperature of $T = 2500$ K and an irradiance of $R_i = 20,000$ W m$^{-2}$. The main fraction of the emitted energy is in the spectral band between 0.8 and 4 $\mu$m. In this spectral region the penetration depths of EVOH and PA are different from that of PET (Fig. 4) and, consequently, the temperature profiles are significantly modified. When the middle layer is thick and located in an external position (Figs. 13E and 14E), this layer absorbs the principal fraction of the infrared radiation, thus leading to an increase of the external temperature. Behind the middle layer, the internal temperature evolution is governed by the very slow heat-conduction process and remains lower. On the contrary, when the middle layer is on the internal side of the preform (Figs. 13F and 14F), the layer collects a large fraction of the radiation and the internal temperature increases.

## CONCLUSIONS

The introduction of layers in PET preform to improve the barrier properties of the final bottle has an impact on the forming process. Effectively, the middle layer whose optical and thermal properties differ significantly from those of PET, changes the heating transfer and consequently the temperature profile. This temperature profile modification is significant with a high-temperature radiator. Unfortu-



**Figure 13**   Profile temperature on PET/PA/PET preform heated by radiator at $T = 2500$ K (thick layer).

nately, this is the case for the heating of a thick preform, which requires a high-temperature radiator, that is, short-wave radiation to obtain a uniform temperature and the rapid heating necessary in the forming process. For the heating stage of multilayer preforms it seems to be preferable to use preforms with the middle layer in the F position and a high-temperature radiator. In this configuration, the infrared oven efficiency increases and the temperature profile in the width of the preform allows a better stretching process.

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